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## Description

The present invention relates to an apparatus for producing a high-purity SiC single crystal by the continuous sublimation and condensation of SiC prepared by vapor-phase synthesis. The apparatus is especially suitable for manufacturing large single crystals.

SiC single crystals produced by the sublimation process are utilised for making devices such as semiconductors in various industrial fields.

In a conventional sublimation process, a powdered SiC material is placed in a graphite crucible having covers, and a seed crystal is attached to the cover plate at a position facing the powder SiC material, which is heated at a temperature of 2000-2500°C. The heated material is evaporated from the crucible and condensed on the surface of the seed crystal. The condensed SiC grows to a single crystal having a crystalline orientation aligned to that of the seed crystal (W. F. Knippenberg, Philips Res.Rep.18,3 [1963] p.171).

In another method, a seed crystal is attached to the bottom of a graphite crucible, a perforated graphite hollow cylinder is located in the crucible, a space between the inner surface of the crucible and the hollow cylinder is filled with powdered SiC material, and the powdered material is heated to a high temperature. The material evaporates and permeates through the holes formed in the hollow cylinder to condense on the surface of the seed crystal at the bottom of the crucible (Y. M. Tairov: J. Cryst. Growth, 43 [1978] p.209; and G. Ziegler, P. Loring, D. Theis and C. Weyrich: IEEE Trans. on Electron Devices, ED-30, 4 [1983] p.277).

The crucible to be used in these methods must be made of high-purity graphite to avoid the resultant SiC crystal from being contaminated with inclusions. Even when graphite material of the highest purity available on the market is used for the crucible, it contains impurities in an amount of approximately 5 ppm. The impurities are evaporated from the wall of the crucible during high-temperature heating, and mixed in the growing SiC crystal. The impurities included in the resulting single crystal cause various problems such as poor performance characteristics and even malfunction, when the single crystal is used to make a semiconductor device.

It is supposed that the impurities in the crucible material are introduced into the single crystal in the following manner. When the powdered SiC material is evaporated in the crucible, the sublimation product, i.e. SiC gas, does not always have a stoichiometric composition, but contains Si, Si<sub>2</sub>, C, SiC<sub>2</sub>, Si<sub>2</sub>C, etc. in a mixed state. These components react with each other to form SiC gas which is consumed for the growth of the SiC single crystal. In addition, SiC is also provided by the reaction of the gaseous components such as Si, Si<sub>2</sub>, SiC<sub>2</sub>, and Si<sub>2</sub>C with C in the wall of the crucible. During the reactions with the crucible, the impurity elements in the crucible are evaporated at the same time and introduced into the growing single crystal.

The graphite crucible itself is also consumed with the evaporation of C, so that the crucible changes its structure and its wall thickness. The changes in the structure and the wall thickness also tend to alter the temperature gradient along the longitudinal direction of the crucible. Consequently, the conditions for crystal growth do not remain constant so that the resulting crystal has poor homogeneity and less reliable quality.

In the sublimation process using a graphite crucible, there are restrictions on the size of a usable crucible and the volume of a powdered SiC material which can be charged in the crucible. Due to the restrictions in the conventional method, it is practically impossible to produce a SiC single crystal having a diameter above approximately 30mm or a length of some tens of millimetres.

On the other hand, single crystals which are larger in both diameter and length are required for enhancing productivity in the processing line of semiconductor devices, and crystals produced in the conventional process are not large enough. Thus production of large SiC single crystals has not been possible hitherto.

Thus the present invention seeks to provide a method and apparatus for producing high-purity SiC single crystals without the use of graphite crucibles. The present invention also seeks to reduce restrictions on the diameter and length of the SiC single crystal product by growing the crystal from SiC synthesised from a gaseous mixture.

Accordingly the present invention provides an apparatus for producing a SiC single crystal comprising a chamber divided into a reaction zone and a crystal growth zone, a conduit for supplying a gaseous mixture into said reaction zone, a reactor tube for synthesising solid-phase SiC from the gaseous mixture, a heater for evaporating the solid-phase SiC, an opening formed in the reactor tube for circulating the evaporated SiC from said reaction zone into said crystal growth zone, a retractable base for mounting a seed crystal thereon and arranged in said crystal growth zone, and heating means for maintaining the interior of said crystal growth zone with a predetermined temperature gradient which reduces from the said opening towards the mounting base, whereby solid-phase SiC synthesised from the gaseous mixture is evaporated

in the reaction zone, circulates into the crystal growth zone and condenses as a single crystal on the seed crystal.

The invention also extends to a method of growing an SiC crystal comprising supplying a gaseous mixture to a reaction zone to form solid phase SiC, heating the solid phase SiC to evaporate it into a crystal growth zone, heating the crystal growth zone to provide a temperature gradient which reduces in a direction away from the reaction zone, and condensing the evaporated SiC onto a seed crystal which is mounted in the crystal growth zone at a position below the reaction zone.

Since the crystal growth is done without using a graphite crucible, high-purity SiC single crystals can be produced with a high degree of freedom on both of diameter and length, without any problems on production or products originated in the crucible. The obtained single crystal is of very reliable quality. The purity of the obtained single crystal is very high, since the solid-phase SiC synthesised by the vapour-phase reaction grows up to the single crystal having less opportunity of including impurities.

The other objects and features of the present invention will be understood from the following description with reference to the drawings attached.

Figure 1 is a schematic view for illustrating an apparatus for SiC crystal growth according to the present invention.

An apparatus for SiC crystal growth according to the present invention has a chamber (10) divided into a reaction zone (20) and a sublimation zone (30). The chamber (10) is supported by a frame (11) equipped with a control panel for various operations.

A conduit (21) is opened to the reaction zone (20), to supply a silane gas, a hydrocarbon gas, a doping gas and a carrier gas, respectively, necessary for the production of SiC. Each gas flows from a gas source to the conduit (21), and its flow is controlled by a flow regulating valve (22a)-(22F), respectively, to provide a gaseous mixture (41) having a predetermined composition. A pressure regulating valve (23) is provided at a position near the reaction zone (20), to control the flow of the gaseous mixture (41) to be introduced into the reaction zone (20). In this way the interior of the reaction zone (20) is maintained at a predetermined gaseous pressure.

The reaction zone (20) has reactor tube (24). The passage of the reactor tube (24) is varied from a large-diameter section to a small-diameter section along the flowing direction of the gaseous mixture (41). A heat insulating member (26) is provided between the reactor tube (24) and an outer wall (25), and a heater (27) is located outside the reactor tube (24). An inner space surrounded with the large-diameter part of the reactor tube (24) serves as a vapor-phase reacting zone (28) for synthesizing SiC. SiC synthesized by the vapor-phase reaction is allowed to flow downwards through a passage (29) surrounded with the small diameter part of the reactor tube (24).

The reactor tube (24) has a projecting part (24a) inserted into the sublimation zone (30). An exhaust pipe (31a) is opened to the interior of the projecting part (24a). Another exhaust pipe (31b) is opened to the lower part of the sublimation zone (30). Pressure regulating valves (32a) and (32b) are provided in the exhaust pipes (31a) and (31b), respectively. A supply conduit (34) equipped with a flow regulating valve (33) is opened to the interior of the sublimation zone (30), to introduce an inert gas such as Ar into the sublimation zone (30).

After the chamber (10) is evacuated, the gaseous mixture (41) having a predetermined composition is supplied through the conduit (21) into the chamber (10) while controlling the pressure regulating valves (32a), (32b), the flow regulating valve (33), etc.. Hereby, each of the reaction zone (20) and the sublimation zone (30) is maintained at a pressure suitable for the synthesis and sublimation of SiC and for the growth of a SiC single crystal. Unreacted gaseous components, e.g. hydrogen and hydrocarbon, among the gaseous mixture (41) supplied to the chamber (10) are discharged through the exhaust pipes (31a), (31b) to the outside.

The sublimation chamber (30) has a heater (35) for heating the interior with a predetermined temperature gradient. Solid-phase SiC (42) flows out from the projecting part (24a) of the reactor tube (24) into the sublimation zone (30), heated by the heater (35) and evaporated. This part of the sublimation zone (30) serves as a sublimator part (36).

A crystal growth zone (40) is provided at the lower part of the sublimation zone (30). In the crystal growth zone (40), there is a mount base (37) for mounting a single crystal thereon. The mount base (37) is supported with a rotary shaft (38) passing through the bottom wall of the chamber (10). The rotary shaft (38) is coupled with an elevator rod (39) extending horizontally from the frame (11). Thereby, the mount base (37) is installed in a state capable of rotating in the crystal growth zone (40) and withdrawing from the chamber (10). Both the rotation speed and the withdrawal speed of the mount base (37) are controlled by operating a control panel (not shown) provided on the frame (11).

The components in the gaseous mixture (41) introduced through the conduit (21) into the reaction zone (20) are reacted with each other in the vapor-phase reacting zone (28) to synthesize the solid-phase SiC (42). The synthesized SiC (42) flows down through the passage (29), out of the projecting part (24a) of the reactor tube (24) and is heated by the heater (35). The heated SiC (42) is evaporated to SiC gas at the sublimator part (36). The formed SiC gas is condensed on a seed crystal (not shown) attached to the mount base (37) in the crystal growth zone (40), under the condition that the environmental temperature is maintained with a predetermined gradient at a constant pressure. Thereby, a SiC single crystal (43) grows on the seed crystal. The rotation speed and the withdrawal speed of the mount base (37) are controlled in response to the growing speed of the SiC single crystal (43), so as to maintain the conditions for crystal growth constant.

The sublimator part (36) is preferably held at the same pressure as that of the crystal growth zone (40) wherein the mount base (37) is located. The pressure in the reaction zone (20) is maintained higher than that of the sublimation zone (30), so as to circulate the synthesized SiC (42) downwards. The temperature of the reaction zone (20) is maintained lower than the sublimation point of SiC, while the projecting part (24a) of the reactor tube (24) is heated at a temperature above the sublimation point of SiC by the heater (35). In addition, the environmental temperature in the sublimation zone (30) is preferably controlled in a manner such that the temperature falls from the sublimator part (36) to the crystal growth zone (40) at a rate of 50 °C/cm or less, to facilitate the growth of the single crystal from the evaporated SiC gas.

Example:

At first, Ar gas was introduced through the conduit (21) and the supply conduit (34) into the chamber (10), to exchange the atmospheric gas in the chamber (10) with Ar gas. The interior of the chamber (10) was then evacuated to 1.32 Pa ( $10^{-2}$  torr.). The supply of Ar gas and the evacuation were alternatively repeated 5 times, to remove inclusions from the chamber (10). Thereafter, Ar gas was re-supplied to the chamber (10), and the interior of the chamber (10) was heated up to 2400 °C by the heaters (27), (35). The interior of the chamber (10) was re-evacuated to 132 Pa (1 torr.) and subjected to 1-hour baking treatment.

After the interior of the chamber (10) was conditioned, the gaseous mixture (41) was introduced in the reaction zone (20) and the sublimation zone (30) both held under the condition shown in Table 1. Said gaseous mixture (41) was one prepared by mixing silane (SiH<sub>4</sub>) gas in a flow rate of 0.3 ml/min, propane (C<sub>3</sub>H<sub>8</sub>) gas in a flow rate of 0.1 ml/min., hydrogen (H<sub>2</sub>) gas in a flow rate of 1 l/min and nitrogen (N<sub>2</sub>) gas in a flow rate of 0.01 ml/min. At the same time, Ar gas in a flow rate of 1 l/min was supplied through the supply conduit (34) into the sublimation zone (30). Hereon, the pressure in the reaction zone (20) was maintained higher than that in the sublimation zone (30).

Table 1

TEMPERATURE AND PRESSURE AT EACH ZONE		
ZONE	TEMP.(°C)	PRESSURE
REACTION ZONE (20)	1200 1400	6670-33000 Pa (50-250 Torr)
SUBLIMATION ZONE (30)	2000 2400	130-100000 Pa (1-760 Torr)
TEMP.GRAIDENT FROM SUBLIMATOR PART (36) TO CRYSTAL GROWTH ZONE (40)		- 15 °C/min

In accompaniment with the growth of the SiC single crystal (43), the mount base (37) was lowered at a speed of 4 mm/hr. while being rotated at a rotation speed of 10 r.p.m. The SiC single crystal (43) grew on the mount base (37). The obtained SiC single crystal (43) was of high quality without the inclusion of impurities. Since nitrogen was used as a doping gas, the SiC single crystal was type-n. The diameter of the SiC single crystal (43) was changed in response to the surface area of the mount base (37) with the high degree of freedom.

Nitrogen gas was used as a doping gas in the example above-mentioned, but of course, other gases may be used which do not provide any doping, or a gaseous material containing a doping gas for producing a p-type single crystal. For instance, a p-type SiC single crystal was obtained by introducing Al(CH<sub>3</sub>)<sub>3</sub> in a flow rate of 0.01 ml/min. instead of N<sub>2</sub>.

In accordance with the preferred features of the present invention as above-mentioned, the solid-phase SiC synthesised in the reaction zone is evaporated and then condensed so that the SiC single crystal grows on the seed crystal, attached to the mount base, as the starting point. Thus the growth of the SiC single crystal can be achieved without using such a graphite crucible as those in a conventional method.

5 Consequently, problems originated in the graphite crucible do not occur, e.g. the migration of impurities from the crucible to the single crystal and the fluctuation in the conditions for crystal growth in accompaniment with the change in the thickness and structure of the crucible. Consequently, a high-purity SiC single crystal excellent in quality can be produced. In addition, there is no restriction on the dimensions of the SiC single crystal to be produced according to the present invention. The single crystal large in diameter or

10 length can be produced under the same conditions.

#### Claims

1. An apparatus for producing a SiC single crystal comprising a chamber (10) divided into a reaction zone (20) and a crystal growth zone (30), a conduit (21) for supplying a gaseous mixture into said reaction zone (20), a reactor tube for synthesising solid-phase SiC from the gaseous mixture, a heater (27) for evaporating the solid-phase SiC, an opening formed in the reactor tube for circulating the evaporated SiC from said reaction zone into said crystal growth zone, a retractable base for mounting a seed crystal thereon and arranged in said crystal growth zone, and heating means (35) for maintaining the interior of said crystal growth zone with a predetermined temperature gradient which reduces from the said opening towards the mounting base, whereby solid-phase SiC synthesised from the gaseous mixture is evaporated in the reaction zone, circulates into the crystal growth zone and condenses as a single crystal on the seed crystal.
2. Apparatus according to claim 1, wherein said conduit is connected to a silane gas source, a hydrocarbon gas source, a carrier gas source and optionally a doping gas source.
3. Apparatus according to claim 1 or claim 2 wherein said retractable base is arranged below the reactor tube and is movable in a downward direction in accordance with the growth rate of the crystal.
4. Apparatus according to claim 3 in which the retractable base has a screw-threaded mounting so that it is simultaneously lowered and rotated.
5. A method of growing an SiC crystal comprising supplying a gaseous mixture to a reaction zone to form solid phase SiC, heating the solid phase SiC to evaporate it into a crystal growth zone, heating the crystal growth zone to provide a temperature gradient which reduces in a direction away from the reaction zone, and condensing the evaporated SiC onto a seed crystal which is mounted in the crystal growth zone at a position below the reaction zone.
6. A method according to claim 5 in which the seed crystal is progressively lowered away from the reaction zone as the crystal grows.

#### Patentansprüche

1. Vorrichtung zur Herstellung eines SiC-Einkristalls mit einer Kammer (10), die in eine Reaktionszone (20) und eine Kristallwachstumszone (30) unterteilt ist, einer Leitung (21) für die Zuführung eines gasförmigen Gemisches in die Reaktionszone (20), einem Reaktorrohr für die Synthesisierung von SiC in fester Phase aus dem gasförmigen Gemisch, einem Erhitzer (27) für die Verdampfung des festen SiC, einer in dem Reaktorrohr ausgebildeten Öffnung für die Zirkulation des verdampften SiC aus der Reaktionszone in die Kristallwachstumszone, einer in der Kristallwachstumszone angeordneten, einziehbaren Basis für die Anbringung eines Kristallkeims auf ihr, und Heizeinrichtungen (35) zur Aufrechterhaltung eines bestimmten, von der genannten Öffnung zur der Anbringungsbasis abnehmenden Temperaturgradienten im Inneren der Kristallwachstumszone, wodurch das aus dem gasförmigen Gemisch synthetisierte feste SiC in der Reaktionszone verdampft wird, in die Kristallwachstumszone zirkuliert und als Einkristall auf dem Kristallkeim kondensiert.
2. Vorrichtung nach Anspruch 1, bei der die Leitung an eine Silangasquelle, eine Kohlenwasserstoffgasquelle, eine Trägergasquelle und wahlweise eine Dotiergasquelle angeschlossen ist.

3. Vorrichtung nach Anspruch 1 oder Anspruch 2, bei der die einziehbare Basis unter dem Reaktorrohr angeordnet ist und entsprechend der Wachstumsgeschwindigkeit des Kristalls in Abwärtsrichtung beweglich ist.
- 5 4. Vorrichtung nach Anspruch 3, bei der die einziehbare Basis mittels Schraubengewinde angebracht ist, so daß sie gleichzeitig abgesenkt und gedreht wird.
5. Verfahren zur Wachsen eines SiC-Kristalls, bei dem man ein gasförmiges Gemisch zur Bildung von SiC in fester Phase einer Reaktionszone zuführt, das SiC in fester Phase erhitzt, um es in eine Kristallwachstumszone hinein zu verdampfen, die Kristallwachstumszone zur Schaffung eines in Richtung von  
10 der Reaktionszone weg abnehmenden Temperaturgradienten erhitzt, und das verdampfte SiC auf einem Kristallkeim kondensiert, der in der Kristallwachstumszone an einer Stelle unterhalb der Reaktionszone angebracht ist.
- 15 6. Verfahren nach Anspruch 5, bei dem der Kristallkeim beim Wachsen aus der Reaktionszone zunehmend abgesenkt wird.

#### Revendications

- 20 1. Appareil pour produire un monocristal de carborundum (SiC), comprenant une chambre (10) divisée en une zone de réaction (20) et une zone de croissance de cristal (30), un conduit (21) pour alimenter un mélange gazeux dans la zone de réaction (20), un tube de réaction pour synthétiser du carborundum en phase solide à partir du mélange gazeux, un réchauffeur (27) pour évaporer le carborundum en phase solide, une ouverture formée dans le tube de réaction pour acheminer le carborundum évaporé  
25 de la zone de réaction à la zone de croissance de cristal, un plateau porte-germe rétractable sur lequel on monte le germe de cristal et qui est aménagé dans la zone de croissance de cristal, et un moyen de réchauffage (35) pour maintenir un gradient de température donné à l'intérieur de la zone de croissance de cristal, ce gradient de température prédéterminé se réduisant à partir de l'ouverture vers le plateau porte-germe, dans lequel appareil le carborundum synthétisé en phase solide à partir du  
30 mélange gazeux s'évapore dans la zone de réaction, s'achemine vers la zone de croissance de cristal et se condense sur le germe pour former un monocristal.
2. Appareil selon la revendication 1, dans lequel le conduit (21) est branché sur une source de gaz silane, une source d'hydrocarbure gazeux, une source de gaz porteur et le cas échéant une source de gaz dopant.  
35
3. Appareil selon la revendication 1 ou la revendication 2 dans lequel le plateau porte-germe rétractable est aménagé en-dessous du tube de réaction et peut se déplacer vers le bas en fonction de la vitesse de croissance du cristal.  
40
4. Appareil selon la revendication 3 dans lequel le plateau porte-germe rétractable comporte un montant fileté de façon à ce qu'il puisse être abaissé et mis en rotation simultanément.
5. Procédé de croissance d'un cristal en carborundum constitué par une alimentation d'un mélange  
45 gazeux vers une zone de réaction pour former du carborundum en phase solide, suivie d'un réchauffage du carborundum en phase solide pour le faire s'évaporer dans la zone de croissance de cristal, puis d'un réchauffage de la zone de croissance de cristal pour établir un gradient de température qui se réduit dans la direction qui s'éloigne de la zone de réaction et ensuite condensation du carborundum évaporé sur le germe de cristal monté sur le plateau porte-germe dans la zone de  
50 croissance de cristal placé en-dessous de la zone de réaction.
6. Procédé selon la revendication 5 dans lequel le germe de cristal s'abaisse progressivement en s'éloignant de la zone de réaction au fur et à mesure que le cristal croît.

FIG.1

